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Analysis of Nitroguanidine in Aqueous Solutions by HPLC with Electrochemical Detection and Voltammetry

D. L. Manning
M. P. Maskarinec

Supported by

U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
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Project Officer: Mary Ann Ryan

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This study was directed towards the analysis of nitroguanidine in aqueous solutions. Nitroguanidine, which is the strongest organic base known, is used in the manufacture of some explosives. A method based on reverse phase HPLC with reductive electrochemical detection was developed for the determination of low levels of nitroguanidine. The nitroguanidine can be concentrated in the aqueous solutions by rotary evaporation at 50°C. If the samples are not too complex, the nitroguanidine can be measured directly by voltammetry. From voltammetry, it was established that nitroguanidine is reduced via an irreversible diffusion controlled four electron process.

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ANALYSIS OF NITROGUANIDINE IN AQUEOUS SOLUTIONS BY HPLC WITH ELECTROCHEMICAL DETECTION AND VOLTAMMETRY

D. L. Manning and M. P. Maskarinec

Analytical Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

FINAL REPORT

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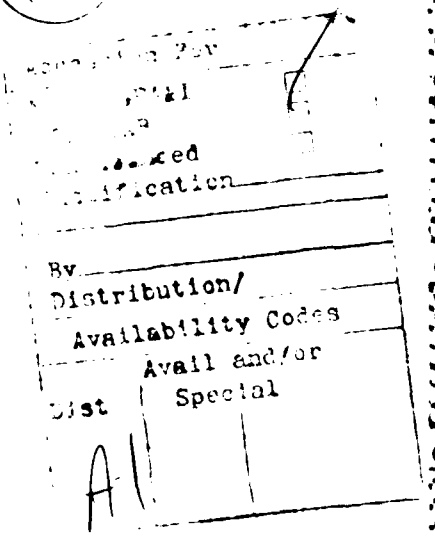

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EXECUTIVE SUMMARY

Explosives components (nitroorganic compounds) continue to be produced in large quantities and therefore are subject to regulations by environmental agencies. These compounds are, for the most part, non-volatile and sparingly soluble in water. The main concern, from an environmental standpoint, thus becomes the contamination of aquifers, both surface water and groundwater.

The objective of this work was to develop analytical methods for the analysis of low concentrations of nitroguanidine in surface and groundwaters. Due to the high polarity of nitroguanidine, the collection of this explosive on solid sorbents failed. However, it was possible to concentrate nitroguanidine in aqueous samples by rotary evaporation at 50°C. The nitroguanidine was analyzed by high performance liquid chromatography (HPLC) with electrochemical detection at a hanging mercury drop electrode (HMDE) positioned at -1.2 volts vs an Ag/AgCl reference electrode. Provided the samples are not too complex, voltammetry, particularly differential pulse voltammetry, offers a rapid, direct and sensitive method for the analysis of nitroguanidine. From voltammetry, it was established that nitroguanidine is reduced via an irreversible diffusion controlled 4 e^- process.

TABLE OF CONTENTS

	Page
EXECUTIVE SUMMARY	1
LIST OF TABLES	4
LIST OF FIGURES	5
INTRODUCTION	7
EXPERIMENTAL	7
RESULTS AND DISCUSSION	8
REFERENCES	15
DISTRIBUTION LIST	17

LIST OF TABLES

Table		Page
1	Analysis of Nitroguanidine in Water Following Concentration by Rotary Evaporation	11
2	Analysis of Water Samples for Nitroguanidine	12
3	Effect of Scan Rate on the Peak Current of the Reduction of Nitroguanidine	14

LIST OF FIGURES

Figure		Page
1	HPLC Separation of Nitroguanidine, HMX and RDX with Electrochemical Detection	10
2	Cyclic and Differential Pulse Volatmmograms of Nitroguanidine (0.19 mM) at HMDE in Aqueous Solution Containing 0.1 M KNO_3 Supporting Electrolyte	13

INTRODUCTION

Nitrated organic compounds are the most widely used explosives components. These compounds have been and continue to be produced in large quantities, and are therefore, subject to regulation by environmental agencies. For the most part, these compounds are nonvolatile but sparingly soluble in water. The main concern, from an environmental standpoint, thus becomes contamination of aquifers, both surface water and groundwater, in and near facilities producing, handling, and storing explosives. While various toxicology studies have been carried out on these compounds (1-5), there exists no definitive toxicology data base for the establishment of acceptable levels of aquifer contamination. Furthermore, reliable analytical methodology for the determination of these components in aqueous samples is lacking.

We have previously reported on the application of solid sorbent collection techniques to the analysis of several explosives in water by high performance liquid chromatography (HPLC) with reductive electrochemical detection (6). This report summarizes our results on the determination of nitroguanidine in aqueous samples by HPLC/electrochemical detection (EC) and voltammetry. Nitroguanidine can be produced from guanidine, which is the strongest organic base known (7). Nitroguanidine is used as a component of some munitions. It is about as powerful as 2,4,6-trinitrotoluene (TNT) and explodes without producing a flash (7). While elaborate procedures have been developed for the analysis of process streams for the production of this substance (8), there appears to be a limited number of analytical procedures for the measurement of low concentrations of nitroguanidine in surface and groundwaters. In addition, the relatively high solubility of nitroguanidine in water indicates a high probability of contamination of the aqueous environment.

EXPERIMENTAL

All solvents used were "distilled in glass" grade, residue free (Burdick & Jackson Laboratories, Muskegan, MI).

Nitroguanidine [$H_2NC(NH_2)$=N-NO_2] Fluka AG, Chemische Fabrik CH-9470, Buchs.

The stock solution is prepared by dissolving 100 mg in 100 mL ethanol and is stored at 4°C.

Reagents

0.025 M Sodium acetate, pH 6. Sodium acetate (4.1 g) is dissolved in 500 mL distilled water, adjusted to pH 6 with acetic acid, then diluted to 2 L with distilled water.

1-Propanol, distilled in glass, Burdick & Jackson

HPLC Mobile Phase

1-Propanol, 0.025 M sodium acetate (pH 6) (30/70 v/v). 1-propanol (300 mL) is added to a 1 L volumetric flask and diluted to the mark with 0.025 M NaAc solution. This solution is filtered through a 0.45 μm Nylon-66 filter and added to the 2 L flask for pump A. For 20/80 (v/v), 1-propanol (200 mL) is added to a 1 L volumetric flask, and diluted to the mark with 0.025 M acetate solution. This solution is filtered through 0.45 μm Nylon-66 filter and added to a 2 L flask for pump B.

Apparatus

Electrochemical detectors used in this work were a Bioanalytical Systems (BAS) Model LC4B (17-D) dual electrode detector and an EG&G Princeton Applied Research (PAR) Model 310 polarographic detector and (PAR) Model 174A polarographic analyzer.

The BAS detector was a BAS TL-6A thin layer cell assembly which consists of a gold-mercury working electrode, stainless steel counter electrode and an RE-1 Ag/AgCl reference electrode. The reference electrode is housed downstream in an RC-2A reference electrode compartment. The PAR detector consists of a hanging mercury drop electrode (medium size).

The LC column was a 25 x 0.46 cm C18 (5 μm particle size) Dupont Zorbax column. The injection valve was a Rheodyne Model 7120 fitted with a 20 μL loop and mounted vertically for sample degassing similar to the method proposed by Lloyd (9). A Hewlett-Packard Model 7045 A X-Y recorder and a Hewlett-Packard Model 3390 A reporting integrator were used for data collection/readout.

A Perkin-Elmer Series 2 liquid chromatograph was fitted with the essential dissolved solvent oxygen removal apparatus for both pumps (10,11). A BAS Model MF 4000 flow through pulse damper was installed between the pump outlet and injection valve.

The mobile phase was deoxygenated by purging with helium at approximately 120 mL/min for 30 minutes followed by continuous sparging at 2-4 mL/min.

RESULTS AND DISCUSSION

Due to the high polarity of nitroguanidine, solid sorbents which were previously used to collection explosives from water (6) were not applicable to nitroguanidine. These included Porapak-R, Porapak-S, XAD-4, and Carbopack-B. Solvent partition with methylene chloride

failed as well. However, it was possible to concentrate nitroguanidine in water samples by rotary evaporation at 50°C, due to the low volatility of this compound. A four day replication study of samples of laboratory water fortified with nitroguanidine is shown in Table 1. The volume of aqueous sample which was reduced to a final volume of 10 mL was within the range 100-250 mL depending upon the concentration of nitroguanidine. In general, reasonable and consistent recoveries were realized over the concentration range tested. Thus, rotary evaporation appears to be an effective way to preconcentrate nitroguanidine in very dilute (μg/L) aqueous samples.

The chromatographic separation of nitroguanidine from other polar explosives such as HMX* and RDX** is shown in Figure 1. As noted, the explosives are adequately resolved. However, the nitroguanidine is not well retained by the column and elutes first. For aqueous samples containing other highly polar, electroreducible substances, interferences (either organic or inorganic) could be a potential problem.

The reduction potential of nitroguanidine is about -1.2 V vs Ag/AgCl reference electrode. This makes nitroguanidine the most difficult of the explosives to reduce and negates to some extent the selectivity of the electrochemical detector.

Various water samples from an army ammunition site (Sunflower Army Ammunition Plant) were shipped to ORNL and analyzed for nitroguanidine to further validate the methodology for this compound. The results are presented in Table 2.

Sample 1 was analyzed directly. Samples 2-6 were analyzed after concentration. Sample 7 was diluted prior to analysis. While no reference data were available, the data generated are within historical limits for these particular sampling points at Sunflower Army Ammunition Plant (SAAP).

Voltammetry allows a rapid and direct, yet reasonably sensitive method for analysis of explosives in water. The trinitroaromatic compounds such as tetryl and TNT are the easiest to reduce. These are followed by the nitrate esters such as nitroglycerine and then the nitramines such as HMX, RDX and nitroguanidine. Voltammetric analysis is applicable to mixtures, provided these mixtures are not overly complex. The governing factor is the relative difference in the reduction potentials of the components.

---

*HMX = cyclotetramethylenetetranitramine
**RDX = hexahydro-1,3,5-trinitro-1,3,5-triazine

Column: Dupont Zorbax ODS (5μ)
Mobile Phase: 1-propanol: 0.025 M Acetate buffer, ph 6.0, (20:80)
Flow: 0.5 mL/min
Inj. Vol.: 20 μL
Detection: Au/Hg electrode @ -1.2 V vs Ag/AgCl
Peak: 1 Nitroguanidine, 2 mg/L
2 HMX, 2 mg/L
3 RDX, 2 mg/L

Figure 1. HPLC Separation of Nitroguanidine, HMX and RDX with Electrochemical Detection.

Table 1

Analysis of Nitroguanidine in Water Following Concentration by Rotary Evaporation

Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
		REPLICATE 1 DATA	
Nitroguanidine	20	9	47
	40	25	63
	80	68	85
	200	166	83
	400	412	103
		REPLICATE 2 DATA	
	20	11	53
	40	25	62
	80	86	108
	200	138	69
	400	448	112
		REPLICATE 3 DATA	
	20	13	66
	40	20	51
	80	76	95
	200	140	70
	400	328	82
		REPLICATE 4 DATA	
	20	12	60
	40	19	48
	80	70	87
	200	240	120
	400	384	96

Cyclic and differential pulse voltammograms for the reduction of nitroguanidine are shown in Figure 2. This substance yields a well-defined irreversible reduction wave at about -1.2 volts vs an Ag/AgCl reference electrode. The increase in magnitude of the differential pulse voltammogram is apparent. The data read-out is presented as a peak for differential pulse polarography which is a very sensitive technique useful in a wide variety of analytical applications. Problems such as polarographic maxima, poorly defined waves and sloping

Table 2

Analysis of Water Samples for Nitroguanidine

Sample Number	[Nitroguanidine]
1.	4.7 ± 0.4
2.	<0.04
3.	<0.04
4.	0.05 ± 0.02
5.	0.31 ± 0.07
6.	0.08 ± 0.03
7.	2140 ± 220

[Nitroguanidine] = mg/L
N = 3

background baselines are also partially compensated for by differential pulse voltammetry. Cyclic voltammetry, on the other hand, can be carried out faster, typically 100 mv/sec scan rate vs 5 mv/sec sacn rate for differential pulse. Since most instruments are multipurpose, the preferred technique is to obtain the cyclic voltammetric information first, then switch to pulse techniques if needed for increased sensitivity and resolution of voltammetric reduction waves. The samples in Table 2 were analyzed for nitroguanidine by voltammetry and the results were in good agreement with the values obtained by HPLC/EC. Thus, voltammetry offers a rapid and direct way of determining nitroguanidine in aqueous samples where the concentration may extend into the low milligram per liter range.

For an irreversible single sweep voltammogram, the peak current (i_p) is given by (12) as:

$$i_p = 3.01 \times 10^5 n(\alpha na)^{1/2} AD^{1/2} Cv^{1/2} \qquad (1)$$

which shows that the peak current is proportional to the parameters $AD^{1/2}Cv^{1/2}$ as in the case for a reversible electrode process, and also to $n(\alpha na)^{1/2}$ instead of $n^{3/2}$ as for the reversible case. The term (αna) is related to the peak-half peak potential difference (13) by:

$$E_p - E_{p/2} = \frac{1.857\ RT}{\alpha naF} = \frac{0.048}{\alpha na} \text{ at } 25°C \qquad (2)$$

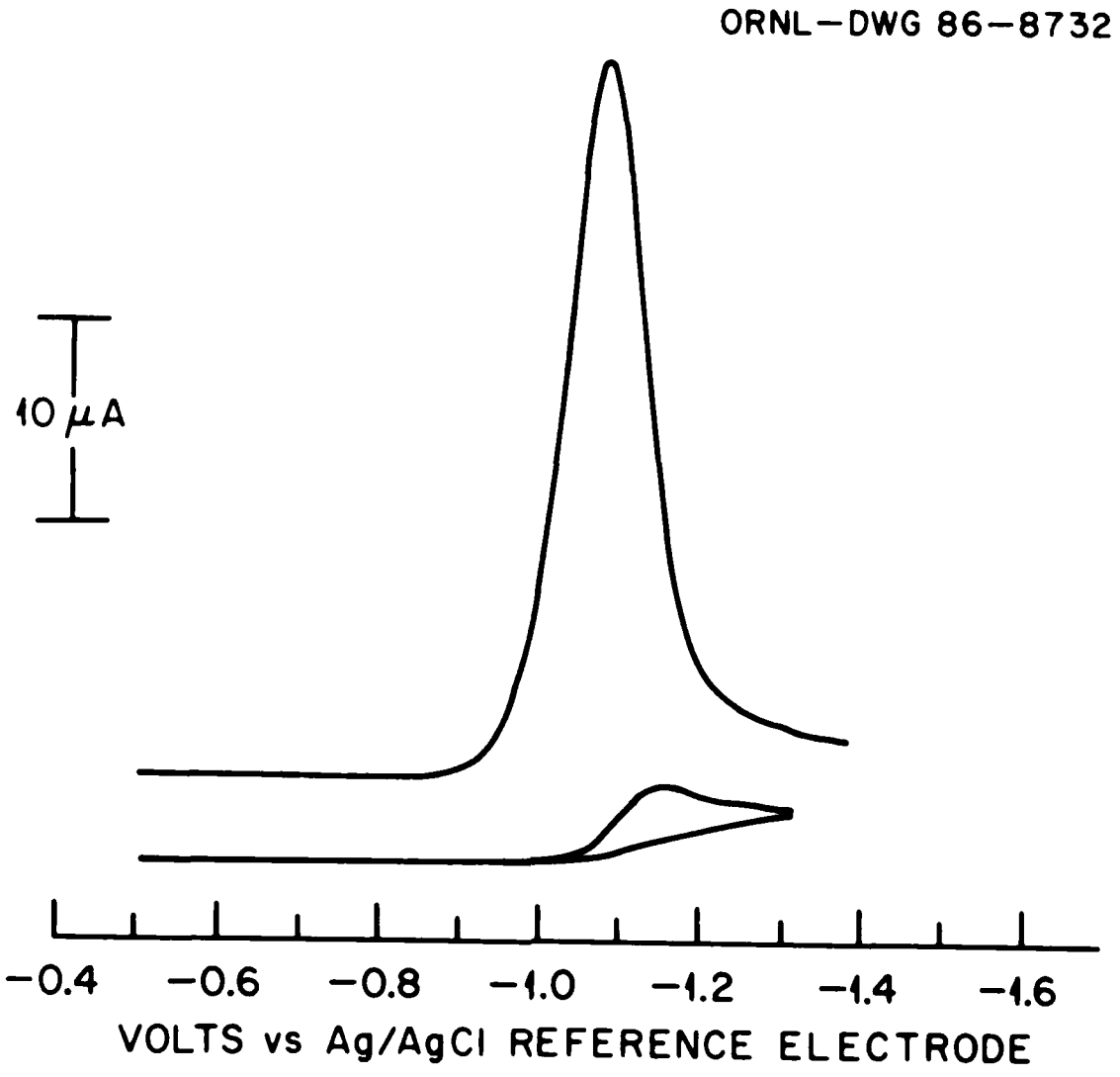

Figure 2. Cyclic and Differential Pulse Voltammograms of Nitroguanidine (0.19 mM) at HMDE in Aqueous Solution Containing 0.1 M KNO_3 Supporting Electrolyte. Cyclic: 100 mV/sec Sweep Rate. Differential Pulse: 100 mV Step, 5 mV/sec Sweep Rate.

where α is the transfer coefficient for the reduction process and na is the number of electrons involved in the activation step. Values of ăna for the reduction of nitroguanidine centered around 0.5 to 0.6. Assuming a value of α = 0.5, the na is approximately 1 for the electrons involved in the activation step. However, this should be considered qualitative in view of the uncertainty in the α value; although α is usually within the range 0.3 to 0.7. The variation of peak current with the rate of voltage scan is shown in Table 3.

Table 3

Effect of Scan Rate on the Peak Current of the Reduction of Nitroguanidine

v V/sec	i_p μA	E_p Volts
0.010	0.8	- 1.220
0.020	1.1	- 1.220
0.050	1.7	- 1.230
0.100	2.3	- 1.240
0.200	3.3	- 1.245
0.500	5.2	- 1.260

Nitroguanidine: 0.192 m M aqueous, 1 percent KNO_3 supporting electrolyte.

Electrode: HMDE, 0.0177 cm^2 Area.

A plot of i_p vs $v^{1/2}$ was linear over the scan rates tested. Taking an average value of αna of 0.55 and a D value of 6 x 10^{-6} cm^2/sec for nitroguanidine, the experimental n value (14) was calculated to be about 3.9 from equation (1). This suggests that nitroguanidine is reduced via a diffusion controlled irreversible 4 electron process. Such a process would be represented as RNO_2 + 4 e + 4 H^+ ---> RNHOH + H_2O. Aliphatic nitrocompounds are known to be reduced at a mercury electrode in this manner (15).

In summary, this work has shown that nitroguanidine can be measured in aqueous samples by HPLC with electrochemical detection as well as voltammetry. Results generated by the two techniques are generally comparable. Concentration of nitroguanidine was effected by rotary evaporation.

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